Serbian Tribology Society

SERBIATRIB '19

16th International Conference on Tribology

Faculty of Engineering University of Kragujevac

Kragujevac, Serbia, 15 – 17 May 2019

CONSIDERATIONS FOR THE SELECTION OF MATERIALS FOR ELECTRICAL SPARK AND GAS FLAME SPRAYING DEPOSITION ON STRUCTURAL STEELS

T. PENYASHKI[1*], M. KANDEVA[2,3], G. KOSTADINOV[1], E. DIMITROVA[1], I. MORTEV[1]

[1]Institute of Soil Science Agrotechnologies and Plant Protection "N. Pushkarov", Agricultural Academy – Sofia, Bulgaria
[2]Faculty of Industrial Technology, Tribology Center, Technical University – Sofia, Bulgaria,
[3] South Ural State University, 76 Prospekt Lenina, Chelyabinsk, Russia
* Corresponding author: peniashki@abv.bg

Abstract: *The aim of the present work is to identify and formulate the basic principles and approaches for the selection of materials for electrical spark and gas-flame stratification of structural steels. For this purpose, have been examined:*
-The characteristic features and physical foundations of the two methods, the changes in the composition and structure of the coating materials in the transfer process and in the formation of the coatings and the general similarities and differences.
- The regularities of formation and qualitative characteristics and properties of the coatings obtained, depending on the process parameters of the coating mode and the layering material.
- The interrelation between: the process parameters of the application system; the coating material; the quality characteristics, the composition, the structure of the coatings; the mechanical and the tribological properties of the coatings.
The requirements for coatings have been formulated for various loads and wear cases and on this basis the requirements for the layering materials are determined by the two methods. Appropriate materials and compositions are specified for various cases of friction and wear. The main approaches to the selection of the layering materials are described.

Keywords: *electrical discharge deposition, gas flame spraying coatings, laminating materials, wears resistance.*

1. INTRODUCTION

The need to increase the complexity, power and efficiency of the technical systems has led to a sharp increase in the social and economic importance of processes related to friction and wear and the providing high wear resistance to the work surface of the bodies. Increasing of wear resistance in the largest extent is achieved through the development of new, environmentally friendly technologies for the deposition of highly effective and reliable coatings for the protection and hardening of metal products. The coating applied to the working surfaces of the parts is a quite versatile and easy means by which it is possible a new approach to the problems of improving the properties of the materials, increasing their working capacity and controlling the friction or cutting processes.

Most of the existing methods and technologies for applying wear-resistant coatings however are realized through complicated and expensive equipment and require high investment. Because of its simplicity and versatility the electrical spark - ESD and gas flame spraying – GFS with their accessible and portable equipment, easy technology and a universality are not only more widespread, but also significantly cheaper, and fully accessible to most consumers [1-5, 6-8].

The common feature of both methods is that the coatings are obtained by transferring the coating materials onto the substrate mainly in liquid and semi-solid (softened phases) as a result of high temperature impact with concentrated energy streams - electro-spark plasma discharge channel and gas-flame jet. Diffusion processes flow in the "substrate - coating" boundary at the methods of thermal impact, are formed chemical compounds, solid solutions and new phases, and the structural construction changes and occurs a transition zone in which runs a grouping of various atoms and reducing of the differences in the properties of the pair materials[1.2, 6-8] .

This ensures a stronger connection with the base than the other methods and makes them more suitable for working with high and variable impact loads. The effectiveness of these two methods for applying coatings is determined by the use of deposition materials, which must ensure, on the one hand, the technological effectiveness of the coating process, and on the other, a high level of physical, and operational properties of the surface.

The wrong choice of material for the application of wear-resistant coatings does not allow obtaining a satisfactory combination of the required level of performance characteristics of tribosystems with acceptable process ability, maintainability and cost-effectiveness of the processes of manufacturing and repairing parts. Numerous and various data are available in the literature on studying of the structure, composition and properties of wear-resistant coatings applied by both methods [1-5,6-8,9-17] and many others. There the basic principles of the formation of the coating are given, and numerous data on their properties, the nature, and type of wear and tear in different conditions, and the results of their application taking into account the 1.3 to 10 and more times the increase in durability. Nevertheless, the processes and the wear mechanism under different friction conditions are still not well understood and there is insufficient data on the relationship between the type and nature of the wear and the physico-chemical and physico-mechanical properties of the coatings.

There are no developed criteria for the selection of materials and layering regimes, and the famous criteria and experimental data do not solve the problem of obtaining quality coatings with high physico-chemical and performance properties. These makes it difficult for the development of a common methodology and recommendations for selecting a coating material and their application in practice. These limits more widespread use of these two so light and accessible methods as a means of extending the life of the products and of machines, and the economy of labor, energy, and materials. In order to improve the efficiency of ESD and GFS, it is necessary to select special materials for obtaining coatings with enhanced quality characteristics and properties and for direct and multi-purpose intended.

In this regard, the aim of the present work is to identify and formulate some basic considerations, principles, and approaches in the selection of materials for electro-spark ESD and gas-flame spraying GFS deposition of structural steels.

2. CHARACTERISTICS OF THE TWO METHODS

Electrical spark deposition / ESD / is the easiest, simplest, cheapest, most versatile and effective means of locally application of a wear-resistant coatings of various uses with different functions on the work surface of rapidly of wearing parts and tools. The main advantages of the ESD process compared to other existing coating methods are the simplicity and accessibility of the technology, the cheap and compact equipment, the low cost of materials and the low energy intensity of the process. The ESD makes it possible to apply the coatings in strictly defined locations without the need for means and measures to protect the rest of the surface of the product. The Electrical spark coating has a high adhesion strength to the substrate, a lack of heating and deformation of the material of the substrate, possibility of use and operation without additional mechanical treatment. The method is based on the use of short-term pulsed plasma discharges with controlled energy in the air environment, accompanied by electrical erosion and polar transfer of material from the depositing electrode (anode) on the article cathode. The formation of the layer occurs under conditions of local short-term operation at high temperatures (above 10000 °C) and pressures. As a result of the electric spark discharges occurs melting and evaporation of the particles of the electrodes which, with extremely high speed, strike and stick to the surface of the laminated product. The formation of a hardened surface layer and coating at ESD is a result of complex plasma-chemical, thermal, and mechano-thermal processes occurring on the local surface areas of the workpiece under the influence of the energy of a spark discharge. Diffusion and chemical interaction between the materials of the anode, the cathode and the surrounding medium accurate, and fixed high-temperature states, extremely unbalanced phases, and structures that sharply change the physico-chemical properties of the surface layer are obtained. A coating with a new relief and structure with different from the initial state surface properties is formed which are controlled over a wide range by changing the parameters of the spark discharge and the composition of the electrode material [6-8, 13-17].

The short duration of the electrical impulse of -5-500 µs leads to an extremely fast hardening of the deposited material, which results in a new structured coating showing unique tribological and corrosion efficiency. The method allows the application of coatings with a thickness usually of 3-200µm from any and on any conductive materials, but most often used are hard-alloy composite materials based on WC, TiC and TiN. The hardness of the applied super dispersed top white layer reaches 20.103MPa and the shelf life of the laminated articles increases 1.5-4 and more times [16-21].

Depending on the layering modes and the materials of the electrodes, coatings can be obtained with predetermined qualitative characteristics, composition, structure, and properties. With an increase in the energy of the single pulse E (current, voltage, capacity, pulse duration), and the pulse frequency, the transfer from the electrode increases, the thickness increases, but also the roughness and the unevenness of the coatings [6-8, 14, 15, 16, 21-23].

The amount of amorphous phase's decreases due to the elevated surface temperature of the cathode reduces the cooling rate of the molten and evaporated particles of electrode material, which activates the transition from the metastable amorphous to the thermodynamically stable crystalline phase. The process does not require special cameras, booths, or operator protection, does not release hazardous waste, smoke or waste water, and is attractive to a very wide range of applications to of strengthening of any rapid wearing tools, working bodies and parts of metallic materials.

The main disadvantage of electrospark hardening is that with an increase in the thickness of the applied coating, its roughness increases, which negatively affects its performance properties.

3. GAS-FLAME SPRAYING

Gas-flame spraying GFS is realized by converting the casting material into molten particles which are applied at high speed to the surface of the coated article and bonded thereto. The application is carried out by means of a torch in which the inserted coating material is introduced and mixed with the burning gas. The molten particles are applied at a rate of 100-150m/s and adhere to the surface of the substrate to form the coating.

The particles carried by the flame stream pass into a plastic and semi-plastic state and after contact with the substrate due to the high kinetic energy, they deform, to form thin flaps of different shapes.

Through this method, coatings with high hardness and wear resistance of all materials on non-metallic and metal surfaces with thickness up to several millimeters are applied. These coatings usually require additional treatment because they are uneven and high roughness. Due to the substrate heating in the application process and the need for post-processing, GFS significantly complicates the technology of layering the cutting tools and heat-treated parts and is therefore mainly applied to unprocessed steel parts of structural carbon and alloy steels.

GFS methods have very broad possibilities both for restoration of worn parts and for production of new ones with predetermined surface properties independent of the properties of the base material. The relatively low speeds of the sprayed particles and the high content of oxides in the coatings formed by the gas-flame method, however, reduce their quality.

A variety of GFS are technologies and devices for high-speed supersonic flame plating systems (HVOF), where the leakage gas stream is 3 to 5 times the sound velocity. With these systems, thick and dense coatings with low porosity and high adhesion strength high bond strength due to the large kinetic energy of the particles are obtained [2,5,11,25-27]. Their thickness may vary between 100µm and 1mm and above, depending on the type of the layered material, as typical thicknesses are in the range 120-500µm [5,11,27].

The main parameters of the process determining the quality, composition, structure and properties of the coatings are: the thermal power emitted in the working jet (Gas flow temperature is - 3000 - 3500˚C); type, pressure and consumption of the working and transport gases; granulometric composition, consumption, particulate form of the starting powder; angle and way of delivery of the powder; roughness, purity and surface temperature of the substrate; type of the surrounding environment [1, 2, 5,11,27].

In spite of the established legalities in the literature between the technological, microstructural and operational parameters, due to the complexity of the processes and the variety of thermal spray technologies and coatings, there is not yet a generic model with which to plan the technological conditions for to produce coatings with predefined properties.

The comparative characteristics of the coatings obtained by the two methods are given in Table 1.

In the manner of transferring the layered material onto the substrate, these two methods are similar, but there are also significant differences. At ESD material was transferred to a liquid, solid (softened) and vapor phases at a rate of the particles with an order of magnitude higher than those at GFS.

The same is mixed with the locally melted micro spot of the substrate to form a surface layer of a mixture of the two materials, new compounds and phases derived from their chemical interaction and from the reactions with the materials from the environment. The coating-substrate bond is diffusion and metallurgical. Adhesion is at the strength level of the substrate. Due to the extremely high cooling rate of the resulting coating has a superdispersed structure reaching to the metallic glass. Its thickness in the most frequent cases is limited - up to 100µm. As a result, a new layer is obtained which is different properties - increased hardness, wear - and corrosion resistance, etc., controlled extensively by the parameters of the spark plasma discharges and the material of the electrodes.

In the case of GPL, the material is transferred to the liquid and softened phases. On the "layer-substrate" borderline is obtained diffusion layer but is absent superdispersed and amorphous non-porous structure, smaller is the degree of mixing of the two materials, and to obtain an acceptable adhesion is necessary pre-heating of the substrate. However, the thickness of the coating can be up to 2 mm, much higher than the ECD, which gives priority to this method of restoring worn surfaces. The roughness of the resulting coatings is higher and in most cases they require further processing.

Table. 1. Comparative characteristics of the coatings obtained by ESD and GFS methods

Energy Source	Temperature ^0C	Minimum area of heating [mm^2]	Maximum energy density in the heated spot [W/mm^2]	Coatings			
				Thickness [µm] Roughnes [µm]	Hardness	Coating properties	Surface to be treated. Size and shape of the part
Gas flame	3000 ÷ 3500	≈1	5×10^2	50÷1300 5÷30	HRC 30-÷70	wear-, corrosion-resistant, heat-resistant	local application, dimensions and form of the part are not limited
Electro-spark discharge	5000 ÷ 15000	$≈1 \times 10^{-6}$	$10^6 ÷ 10^9$	5÷500 1÷12	HV 7÷18GPa		

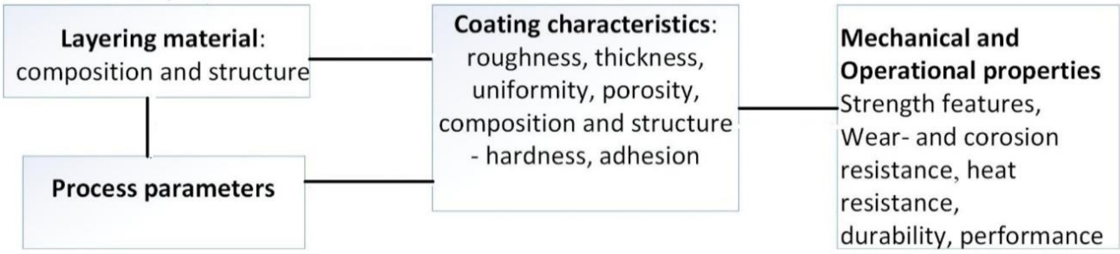

Figure 1. Correlation scheme "layering mode and material - wear resistance"

ESD is better suited for preliminary surface modification and the GFS- for recovery and in this sense, the two methods complement each other.

4. FACTORS DETERMINING THE DURABILITY OF THE COATED PRODUCT:

In both methods, the durability and exploitation properties of the layered products depend on the simultaneous action and mutual influence of a large number of factors, which are divided into three main groups:

- Factors relating to the layering conditions - the layering mode parameters, the layering material, the coating application scheme, etc.;
- Factors relating to the layered products - material, type, shape and dimensions of the work parts, the significance and degree of impact on the machine's working, productivity and operating resources etc.;
- Factors resulting from operating conditions - speed, type, nature and size of the mechanical loads, temperature, type of friction, presence of cooling, type and nature of prevailing wear and degree of admissible wear, impact of the environment in the exploitation process, and for friction pairs - the material and type of the conjugate detail.

In both methods, the composition, the structure and the properties of the deposited coatings depend on the type, composition, and structure of the deposited and of the substrate materials and the parameters of the application regime. Their interconnection is given schematically in Fig 1.

It can be seen from the diagram that in both methods the main factor is the type of material to be laid. From the selection of the material combined with the parameters of its application regime, the properties of the coatings depend - and hence their wear resistance. Of the above factors depends the choice of both the material and the method of coating. If it is not known how this complex affects any of the determinant properties, it is not possible to determine the appropriate type of layering material for one or another article.

5. REQUIREMENTS FOR COATINGS AND COATING MATERIALS

In the process of wear, the contacting surfaces must successfully resist on plastic deformations, on shearing of micro-volumes from the material, on the penetration of solid abrasive particles in surface (particles from the external environment, separated particles or growths during adhesion), as well as and against effects of aggressive media and temperatures. Depending on the specific conditions of use, wear-resistant coatings must meet a variety of different requirements. In some cases, high resistance to abrasion wear is required, in others high resistance to heat load, in third - high chemical resistance, etc. In most cases, coatings require a complex of properties that ensure long-term performance of the product under certain operating conditions, the main ones being:

- High wear resistance and maintenance of consumer properties over the entire range of temperature, pressure, or chemical aggressiveness in the working area;
- High micro-hardness is a basic requirement that reflects the resistance of the abrasion-resistant coating;
- Tensile strength and toughness reflect the ability of the coating to withstand stresses and deformations in working conditions, to absorb mechanical energy under dynamic loads, not to break under the influence of high pressure on its surface, to prevent the formation and development of cracks in variable conditions loads, impacts and vibrations;
- Chemical and corrosion resistance, heat resistance, thermal conductivity, low coefficient of friction;
- Technological and economic requirements
- They affect the parameters and the properties of the coating depending on its deposition process, the possibility of obtaining coatings with high quality characteristics - low roughness, high density and uniformity, necessary thickness for the concrete case , with predefined properties, composition , structure and morphology, and the ability to control and evaluate the process. They are crucial in terms of process performance and its cost, the minimizing the cost of parts and coatings at maximizing product durability and productivity;
- An important condition is also the formation of a strong connection between the base and the coating. The nature of the base materials and the particles of the coating and their energy state during bonding are determinant factors for the formation of a strong bond.

5.1. Requirements for coating materials

Additional requirements for coating materials according to the layering processes.

The operability and efficiency of the coated detail can be ensured only if coating material has sufficient hardness, strength, wear resistance, temperature resistance and thermal conductivity and in addition, according to the particularities of the two methods, the following qualities:

- Low degree of oxidation in the transmission process;

ESD and AFS are accompanied by rapid specific chemical-thermal phenomena, occurring at high local temperatures and pressures. These conditions require the laminating material to be less susceptible to high-temperature oxidation processes or to use self-lubricating additives in order for to prevent the formation of oxide and nitride phases, which cause brittleness of the applied layer, [1-3,10,11,25,27-30].

- Possible lower melting temperature (under GFS) of the bonding mass;
- Full or high solubility of the bonding metals in the iron - which is a guarantee of a strong bond with the substrate;
- Resistance to high temperatures and a tendency to form intermetallic compounds, borides, carbides and nitrides in the course of formation of the coating.
- -Smaller grain sizes of the high-hard phases to aid and facilitate their melting;
- At ESD - small grain sizes, up to several microns, contributing to obtaining the ultra-dispersive and amorphous structures.

5.2. Considerations in selecting the composition of the coating materials

For the correct choice of the layering material it is necessary to consider the interconnections: product for coating - operating conditions - laminating material - coating method and process parameters - topography, composition and structure of the coating - physicochemical and mechanical properties of the coating - wear resistance and performance of the covered surface- Fig. 2.

If for the parts working in conditions of static load, the main criterion in evaluating the coated layer, is its wear-resistant, for the products working under dynamic load conditions, is essential this layer to acquires a strength of fatigue and impact strength. Therefore, for the numerous and different operating conditions of different products, it is necessary to create different materials and different composition, structure and morphology coatings.

Just as well as there are no universal constructive or tool materials, there is no and universal coating materials. Traditionally, pure metals and metal alloys are used as deposition materials.

To achieve high adhesion of the coating to the substrate and efficient formation of the layer, the components of the laminating material must form solid solutions or intermetallic compounds with the substrate material and have a thermal expansion coefficient close to it. As most suitable for coatings, most authors [1-3,6,7,9,10,11,15,24,27,28,30,31] and many others indicate Ni, Co, Fe, Cr, Mo, W Cu, Al, Fe, and their alloys. The metals Ni, Co, Cr, Mo, W form with Fe limited and unlimited solid solutions and intermetalides. These metals form intermetallic phases with iron, and carbide phases, therefore so that the probability of increasing the hardness and wear resistance of the layer is high and therefore these metals may be included in the composition of the laminating materials.

The most widely used coatings are chromium-nickel alloys that provide resistance to high-temperature corrosion [1-3, 24, 28, 30-32]. Special attention to the selection of the brazing metals in the composition of the electrodes and powders is separated on chromium Cr. Chromium has a higher wear resistance than iron and particularly high wear resistance in various aggressive environments. Iron and chromium have unlimited solubility in solid and liquid state, regardless of temperature. Most researchers have found that a number of solid solutions are formed in the iron-chromium alloy.

According to some researchers [6,7,9,10,12,15,22,24,29,30,33], the combination of Cr with Ni contributes to the formation of more carbides in the layer and an increase in wear resistance. The heat action on the substrate in the presence of nickel may cause both the solid solution of Ni in the γ - Fe, and the formation of additional compounds of the type of FeNi3, and in the presence and B is possible, and formation of Fe_3Ni_3B.

According to most researchers [1,3,5,7,9,10,22,30,31,33], the Ni and Co metals provide a high density of the layers, forming limited and unlimited hard solutions with Fe and intermetalides.

The Cr has a less complete electronic envelope and therefore has a higher carbon affinity in steels to form carbides, which increase the hardness of the layer as opposed to Ni and Co, which in the presence of Fe do not form carbides. The presence of Co in the steels and alloys leads to high stiffness, corrosion resistance and high resistance to wear. Cobalt is a valuable alloying element for high-speed tool steels.

Combined with chromium, a high hardness of alloy steels is achieved. When creating layering materials, it is also necessary to take into account the influence of the environment and the ability to form carbides and borides directly onto the substrate. For this reason, technological additives such as B, Si, C, Al_2O_3, Cu, C, Al and others can be incorporated into the material composition with different purposes. For example, the introduction of B, Si, C reduces the formation of oxides, and at ESD also reduces the erosion resistance of the laminating electrodes [22, 35-38,39].

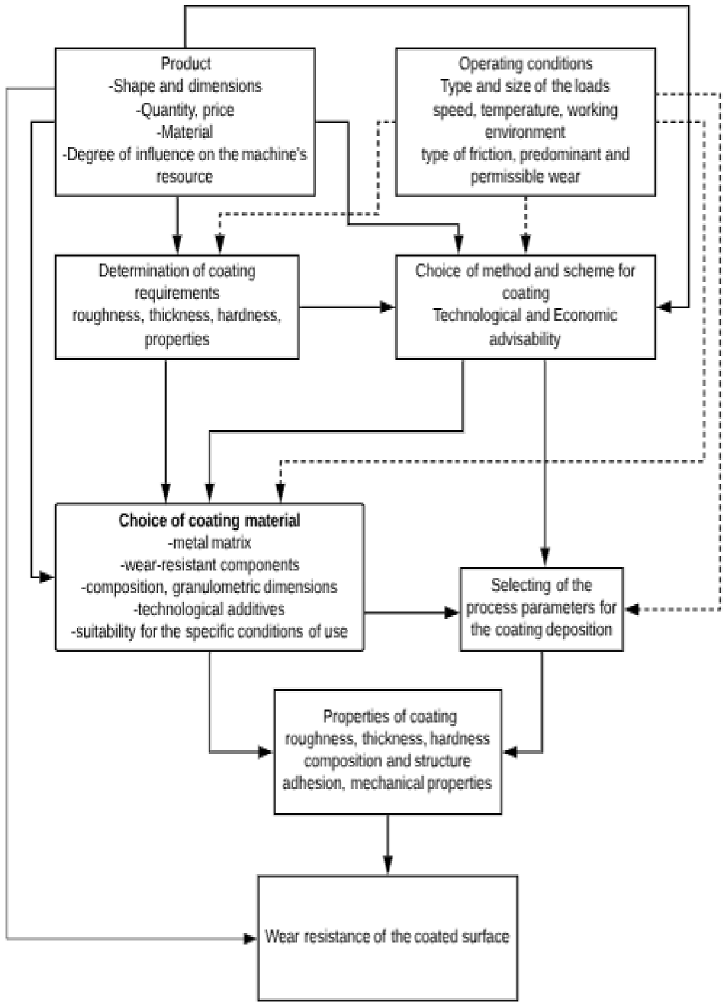

Figure 2. An algorithm for selecting a suitable coating material

At the same time, the boron serves as a donor for the formation of wear-resistant borides in the layer, the carbon - as an anti-decarburization during the transfer process, and for the additional formation of dispersed carbides in the process of forming the coating. Cu contributes to reducing the size of the grains in the layer; Aluminum increases the yield strength limit and, because of its low melting temperature, helps to increase the transfer to the substrate. Due to their good wear and corrosion resistance, Ni-C-rB-Si-based alloys are commonly used in the GFS on steels [35-40]. Essential elements in these compositions are B and Si. These elements have several functions: they reduce the melting temperature of Ni by several hundred degrees - from 1450 to 1000 °C. They form a low melting point boron silicate, which flows to the surface and protects the melt pool from oxidation. Further, they promote wetting of the substrate by reducing Ni, Co, Fe and Cr oxides, controlling surface tension and fluidity of the melt .The low melting point of NiCrBSi alloys as well as the fluxing effect of the Si and B allows these materials to be deposited by flame spray followed by fusing and welding the powders. An increase in the amount of chromium, boron and carbon increases the amount of solid carbides and borides, respectively [15, 35-40].

In addition to nickel-based, higher wear-resistant cobalt-based metal alloys Co-Ni-Cr-B-Si can also be used. In this case, in order to increase the bond strength and the degree of melting of high-hard phases, a higher heat capacity of the flame jet at the GFS is required, and at the ESD process, impulse parameters will depend on the quality requirements of the coatings. In spite of such widespread use of Ni-Cr-B-Si alloys in thermal spraying, their abrasive wear resistance is still not fully understood.

The insufficient wear resistance of metal coatings leads to the need to use new materials for the ESD and GFS. The development of chemistry and nanotechnology allows us to accept the particularly high performance of complex coatings, from composite materials that have unique properties. According to most of the authors, the future is of the compositional coatings. These are multi-component multi-phase coatings from several of the above materials - mixtures and solid solutions of metals and metal-like compounds - mainly carbides, borides, nitrides and oxides of difficult metals. They are the most common combination of two or several heterogeneous materials. In the hardened surface layer, it is necessary to ensure sufficient ductility, high hardness, and strength. These requirements can be realized only in the composite coating, organizing a hardened layer consisting of a plastic base (matrix) with solid inclusions.

For a metal matrix Ni-Cr-B-Si and Co-Ni-Cr-B-Si alloys are most suitable - for the latter more appropriate is the HVOF method. Besides Ni, Cr, Si, Co and B, these alloys may contain Fe, C and sometimes Mo, W, Cu.

Experience has proved these alloys are a good choice for components in the presence of hard particles. Higher hardness and abrasion resistance is ensured with additions of hard-alloy compounds [15,22,2,35-40].

In the selection and optimization of the composition of the laminating material should also take into account the change in its properties in the process of the ESD and the GFS. In most cases, the issues about the choice of solid phases can be successfully resolved using components of the difficult compounds of metals of IV-VI groups of the periodic system with boron, carbon, nitrogen and other non-metals. High wear-resistant components in the composition of the composite material are most suitable: WC, TiC, TiN, Cr_2C_3. The authors of this paper also recommend TiB_2 in combination with WC and ultra-hard B4C.

Tungsten carbide based alloys with TiC are of high strength and hardness, they have the widest application in the production of various tools and in the application of wear-resistant coatings on metals. TiC is widely used for wear-resistant coatings on cutting tools. Titanium carbide is recommended because of its wide range of homogeneity, high hardness, temperature resistance and wear resistance. [7,13,15,22,23,31,33,34,42,43].

TiN has the lowest friction coefficient and the highest resistance to wear. Furthermore, it is chemically least active with respect to iron and copper and can be an excellent barrier against adhesion and diffusion wear and is the most common in practice material for applying wear-resistant coatings on metal cutting tools of high-speed steels [13-15,21-23,41-43].

Titanium diboride is distinguished by its very high hardness, abrasion resistance and chemical resistance[41,42]. Boron carbide B_4C is a super hard material with extremely high abrasion resistance and abrasion resistance.

Conventional tungsten carbide alloys can be added in order to increase the amount of WC and cobalt. The WC and TiB_2, in addition to abrasive wear, are also resistant to impact loads [6,7,15,22,31,34,41,42].

Table 2 gives some recommended powder formulations designed and tested by the authors suitable for wear-resistant coatings on steels.

The microstructure of the coatings obtained with the above materials contains besides the metal matrix and different amounts of solid carbides and borides. [5,10,11,12,24,26,39].

Coating composite material consisting of particles of the metal alloy on and or particles of high wear resistance compounds – WC-TiB_2, B_4C is of particular interest since the hard particles as incorporated in the metal alloy matrix give high hardness (1800-2000HV) to the coatings. The test results of these coatings obtained by blending powder mixtures [11,26,39] show that wear sharply reduces and takes up to twice smaller values than those of the coatings of conventional materials without the presence of added our materials. High hard additives in the volume of the coating forming an internal contact network with high strength characteristics, which provide a high resistance of the coating against destruction by scratching action of the abrasive particles.

Table 2. Conditional designation of the coating and suitable powder chemical composition (% by weight)

№	Designation	Chemical composition of powders, wt. %
1	602P - Ni-Cr-B-Si-Fe-C and tungsten carbide.	Cr: 13.2; Si: 3.98; B: 2.79; Fe: 4.6; Co: 0.03; C: 0.63; **Ni: Balance**
2	10611W- Co-Ni-Cr-B-Si and tungsten carbide.	(45% (1.5% C, 1.5% Si, 23% Cr, 0.5% Fe, 42% Co, 30% Ni,1.5% B) + 55% WC)
3	6P50W	Cr: 13.15; Si: 4.28; B: 2.87; Fe: 0.04; Ni: 29.6; Co: 0.04;C: 0.58; **WC+ 12%Co : Balance**
4	WC–12Co,	Co: 12; C: 5.4; Fe: < 0.1; Ni: < 0.1; **WC: Balance**
5	602P–6P50W–(WC–12Co)-(B_4C - TiB_2)	Mixture ratio (1:1:1: 0,3)
6	NWW10T20B10	60% (55% (0.6% C, 2.86% Si, 12% Cr, 3.94% Fe, 77%Ni, 3.6% B) + 45% WC) + 10% WK8 + 10% B_4C + 20%TiB_2.
7	NWW10T10B10 (based on 602P)	70% (55% (0.6% C, 2.86% Si, 12% Cr, 3.94% Fe, 0%Co, 77% Ni, 3.6% B) + 45% WC) +10% WK8 + 10% B_4C + 10% TiB2 (WK8 is hard alloy with 92% WC and 8% Co).
8	KWT10B10 (based on 10612)	80% (45% (1.5% C, 1.5% Si, 23% Cr, 0.5% Fe, 42% Co, 30%Ni, 1.5% B) + 55% WC) + 10% B_4C + 10% TiB_2.

6. DISCUSSE AND FINDINGS IN RELATION TO COATING MATERIAL STRUCTURE

Analyzing the surface hardening, it should be noted that, by increasing the hardness, we reduce the ductility, which reduces the danger of adhesion sticking and micro-welding of the conjugated surfaces, on the one hand. On the other hand, a decrease in plasticity increases the sensitivity to local high pressures, which can even lead to local destruction of the surface.

To reduce the brittleness of the coating and increase the performance of the electrospark and GFS processes, it is advisable to increase the metal binder [3,7,22,28,29,32,39] . The metal bond material must wet the refractory phase of the composite, since in this case the wear-resistant particle is enveloped by a low-melting component, which ensures good adhesion to the alloyed surface.

The metal matrix improves and adhesion with the substrate because at the moment of impact of the particles there is an exothermic reaction that is accompanied by a self-binding. The appropriate amount of the plasticizer phase depends on the chemical and physical properties of the wear-resistant phase and the substrate material and should be optimized for the various difficult-to-wear compounds. If the material of the plasticized phase does not wet the particles of hard phases, the amount it should be higher.

Very important is the determination of the amount of high hard supplements. In a large quantity over 70%, they do not adhere firmly to the substrate and the wear resistance of the coating decreases. This is due to the insufficiently high temperatures reached in the flame of the acetylene torch to melt (albeit only partially) the carbide particles and to embed in the coating.

For example, in the coatings made of the powder NWW10T20B10 [39],only about half of quantity W, Ti and B was found, indicating that about half of the mechanically added to the starting powder WC, TiB_2 and B_4C particles (with a concentration of 40 wt%) do not participate in the construction of the gas-flame coatings.

At ESD, however, due to the high temperatures of the process, the amount of high-hard additives in coating is a pretty greater.

Considering that these additives increase the hardness but also the brittleness of the coating and the specificity of the ESD transfer, the optimal concentration of the bonding mass should be in the range of 12-25% for coatings of different uses, and for thick coatings - 20-40%. [6,7,8,13-16,22,23,33,43]. The composition and particle size is chosen depending on the type of the material to be laid, the desired coating properties and the type of the coating apparatus.

For dust of metals and alloys, the most authors are recommended that particle sizes be between 45µm and 105µm, and for powders of hard-wearing oxides and carbides between 10µm and 40µm [1,3,4, 5,10,12,24,25,27,29].

In practice, such layers deposited on steel substrates can be used to increase hardness and wear resistance during high load and friction conditions of in abrasive environments as well as for corrosion-resistant workpieces. Obtaining a dense and uniform coating with each of the materials used requires certain parameters of the application modes.

Table 3. Methods of surface modification and increased durability depending on operating conditions defining the type of predominant wear.

Workingconditions causing predominant wear	***Basic methods and materials for surface modification and increased durability***
Friction with low contact pressures low, medium and high speeds	*Solid antifriction alloys and composites. Improving the surface relief, increased hardness and abrasion resistance - thin and medium single- and multilayer coatings of wear-resistant materials with low coefficient of friction and high smoothness- applied by ESD - with composite electrode materials based on (W, Ti) C, TiC-TiN, TiCN, TiB_2-TiAl with bonding metals Co, Cr, Ni, Mo and different technological additives(Cu, Al_2O_3,B,C); GFS with Ni-Cr-B-Si alloys different technological additives of WC-Co hard alloys, compositions KWW10T10B10 and NWW10T20B20;*
The presence of solid particles and elements causing abrasive wear	*Improving relief and an increase in surface hardness - medium and large single-and multi-layer coatings of hard and abrasive resistant materials - hard alloys- WC-Co, (W, Ti)C, TiCN-II layer, compositions KWT10B10 and NWW10T20B20 applied by ESD, compositions; KWT10B10, NWW10T10B10, 6P50W- by GFS and HVOF methods.*
Adhesive interaction between contacting materials	*Creating a chemical resistance layers to the material of the conjugated detail – hard alloys based on TiN + Al_2O_3, WC-TiC-TiN, TiB_2-TiAl, (W,Ti)C-TiCN+ B_4C, KWW10T20B10 - applied by ESD ; compositions KWT10B10, NWW10T10B10, 602P-10611W–(WC–12Co)-(B_4C - TiB_2)- Mixtures , 6P50W- by GFS and HVOF methods.*
Fixed, variable force and high shock workloads	*Increase in surface hardness, toughness and strength characteristics and improve relief - medium and large single and multilayer coatings of high hard and rubbery materials - hard alloys, WC-B_4C, TiC + TiN, TiC-B_4 C, Ni-Cr-Si-B, TiB_2 - BN, WC-B_4C applied by EH, plasma and gas or electrochemical lamination. Increase in surface hardness, toughness and strength characteristics and improve relief - by medium and large single and multilayer coatings of high hard and rubbery materials - hard alloy based onWC, WC-TiB2,Ni-Cr-Si-B-Fe, , NWW20T10, KWW10T10 applied by ESD,; 602P , 10611W, KWW10T10 ,602P–6P50W – applayed by GFS or HVOF.*
Thermal stresses	*Thin and medium-sized single-and multilayer coatings from temperature-and chemical-resistant materials with a thermal conductivity close to that of the substrate – Co- Cr, hard alloys based on TiN, TiC- TiN+ Al_2O_3, TiAlN, TiC-TiAlN, TiC-TiB_2+B4C, TiB_2-TiAl, - obtained by ESD; 10611, KWW10T10B10, NWW10T10B10 etc- by GFS or HVOF.*
Work in chemically aggressive environments	*Create a layer of thin and medium-sized one-and multilayer coatings of chemically resistant materials – Cr-Ni-Co, hard alloys based on TiC – TiN+ Al2O3, (W,Ti)C -TiB_2, WC-TiB2–B_4C,-obtained by ESD; 10611, Fe-Cr-Al-Mo, KWW10T10B10, Mixture 602P–6P50W–(WC–12Co)+(B_4C - TiB_2), Co-Ni-Cr-B-Si alloy and tungsten carbide. etc.*

To create the necessary physicochemical and mechanical properties of the surface layer for a variety of operating conditions, we need to control the processes involved in depositing the coatings. One of the possible ways to increase productivity and wear resistance of the

ESD coatings is to create amorphous and nanostructured phases. The unique wear resistance, high rigidity and plasticity, good performance of the amorphous and nanostructured alloys are related to the relaxation character of their physical and mechanical properties and are a prerequisite for the appearance of such properties in the electrospray coating.

It was found [40,44,45] that the structure of the electrode material strongly affects the composition, structure and properties of the coating (hardness, modulus of elasticity, roughness, coefficient of friction, wear resistance). When using a nano-structured electrode, the carbide phase (Ti, W) C + W_2C content in the coating increases from 60 to 95%, resulting in an increase in hardness, and the friction coefficient decreases from 0.7 to 0.3.

The lack of reliable scientific data on the properties of coatings with amorphous and nanocrystalline structures, the small number of scientific developments in the field of wear-resistant coatings using amorphous and nanostructural materials, as well as the set of thermophysical and physico-mechanical properties of these alloys, make the obtaining of coatings of such structures a complicated but necessary scientific and technological task.

Table 3 gives the recommended ways of surface modification and coating materials to increase durability according to the operating conditions that determine the type of prevailing wear. From the table is visible that much of the recommended materials combine several qualities.

7. CONCLUSIONS

The hardening methods under consideration have both advantages and certain disadvantages. Their use for parts and tools requires both the improvement of specific technological processes, and at the same time to search for new high effective applying materials taking into account the specifics of their behavior in the process of-of transfer onto the substrate and the knowledge of the complex influence of the materials on the properties and morphology of the coatings, together with the peculiarities and the parameters of the ESD and GFS regimes. Therefore, the development of an effective, fairly simples and economical to industrial production materials improving wear resistance remains an urgent scientific and practical task.

Choice of suitable laminating materials for the particular case should be performed in the following sequence: analysis of the material, shape and dimensions of the product; analysis of the working conditions of the product - prevailing wear and its causes; formulation of the requirements for the coating in order to provide the necessary complex of exploitation properties; determination of possible methods to provide the necessary complex of operational characteristics of coatings; analysis of the relation between the morphology, the composition, the structure and wear and tear, operational reliability and durability of the layered surface, choice of highly resistant and friction materials for coatings and process parameters for their deposition.

Factors influencing the properties of the coatings and the durability of the plastered products have been identified and on this basis the basic requirements for the composition, structure and properties of the coatings and the plastering materials are formulated and certain recommended materials for wear-resistant coatings for different operating conditions are justified.

Based on existing scientific and technical literature:

- it has been found that in order to increase the wear resistance of ESD and GFS coatings it is necessary to use composite materials by adding high solid carbides, borides and nitrides of W, Ti, Cr etc. to the used metal alloys in the type and quantities according to the specific operating conditions;
- indicated are compositions of laminating materials specified for different operating conditions.
- these materials should be applied by appropriate regimes according to the chosen method.

ACKNOWLEDGMENT

The present work is based on researches that are funded from the Bulgarian National Science Fund of the Ministry of Education and Science under the project "Research and Development of New Wear - Resistant Coatings Using Compositional and Nano Materials”.

REFERENCES

[1] L. Pawlowski: *The Science and Engineering of Thermal Spray Coatings*, Chichester: John Wiley & Sons, England, p. 656, 2008.
[2] *An Introduction to Thermal Spray*: Brochure, Oerlikon Metco, Winterthur, 2015.
[3] M.A. Belotserkovskiy: Tribotechnical Characteristics of Gas-flame Coatings: Friction and Wear, Vol. 21, No. 5, p. 534, 2000 (in Russian).
[4] *White Paper of ASM,* International Thermal Spray Society. www.tss.asminternational.org.
[5] Broshures: https://www.flamespray.org, https://syscoat.com, http://www.linde-gas.com, https://www.castolin.com,http://remoterm.com/
[6] G.V. Samsonov, A.D. Verkhoturov, G.A. Bovkun, V.S. Sychev: *Electrospark alloying of metal Surfaces*, Kiev, Naukova Dumka, p. 220, 1976 (in Russian).
[7] A.E. Gitlevich, V.V. Mikhailov et al: *Electrospark, alloying of metal surfaces*, Chisinau, Stinitsa, p. 198, 1985, (in Russian).
[8] R.N. Johnson, G.L. Sheldon: Advances in the electrospark deposition coating process, Journal of Vacuum Science & Technology A, Vol. 4, No. 6, pp. 2740-2746, 1986.
[9] R.J. Wood, K.M. Roy: *Surface Engineering for Enhanced Performance against Wear*. Springer -Verlag Wien 2013. Editors: Roy, Manish. Chapter1-Tribology of thermal-sprayed coatings. pp. 1-43.
[10] G. Barsukov, V.V. Barabash, A.Yu. Rodichev, O. Kozhus: Technology of Powder Coatings Application by Gas-flame Spraying Using Oxyhydrogen Flame, Materials Science Forum, Vol. 906, pp. 80-87, 2017 (in Russian).
[11] I. Peichev, M. Kandeva: Characterizing of Composite Coatings Deposited through Gas-thermal Super Sound Stream (HVOF-Process) at Different Technological Regimes. In: Proceedings of the 12th International Conference on Tribology ‘BULTRIB 2012’, Sofia, pp. 187-197, 2012.
[12] J.Davis (ed.): *Handbook of thermal spray technology*, ASM International, Materials Park, OH, pp. 3-13, 2004.
[13] T.G. Peniashki: Types of coatings and Methodsfor their deposition on the machinetools.Some guidelines for selecting suitable materials and methods for coatings. Tribological Journal Bultrib, pp. 258–286, 2011.
[14] T. Penyashki, G. Kostadinov, I. Mortev, E. Dimitrova: Improving the Surface Properties of Steel 210Cr12 by Non-Contact Electrical Spark Deposition with Electrodes Based of WC and TiC. Journal of the Balkan Tribological Association, Vol. 23, No. 1, pp. 69–81, 2017.
[15] V. Nikolenko, A. D.Verkhoturov, N. Syui: A. Generation and study of new electrode materials with self-fluxing additives to improve the efficiency of mechanical electrospark alloying. Surface Engineering and Applied Electrochemistry, Vol. 51, No. 1, pp. 38–45, 2015.
[16] T.G. Penyashki, G.D. Kostadinov: Enhancing durability and resources agricultural machinery using electrospark hardening. Agricultural Engineering (Bulgaria), No. 4-6, pp. 48-55, 2013.
[17] V.N. Gadalov, D.N. Romanenko, I.M. Goryakin, YU.P. Kamyshnikov, V.I. Shkodkin: Local selective application of electrophysical coatings to metalworking tools. Strengthening technologies and coatings. (Uprochnyayushchiye tekhnologii i pokrytiya). No. 4, pp. 33-36, 2008.
[18] E.A. Brown, G.L. Sheldon, A.E. Bayoumi: A parametric study of improving tool life by electrospark deposition. Wear, Vol. 138, Iss. 1–2, pp. 137-151, 1990.
[19] K.R.C. Soma Raju, N.H. Faisal, D.S. Rao, S.V. Joshi, G. Sundararajan: Electro-spark coatings for enhanced performance of twist drills. Surface & Coatings Technology, Vol. 202, pp. 1636, 2008.
[20] V.N. Gadalov, R.E. Abashkin, Yu.V. Boldyrev, E.F. Balabaeva, A.I. Lytkin: Cutting-tool wear and hardening of high-speed steel by local electrospark coating application. Russian Engineering Research, Vol. 29, Iss. 4, p. 419, 2009.
[21] G.A. Bovkun, Z.I. Vladkova, V. Molyar, T. Penyashki, Yu.G. Tkachenko: Research hardening of steels at a local electrospark depostion of metal carbides, Surface Engineering and Applied Electrochemistry, No. 1, pp. 10-12, 1988 (in Russian).
[22] A.D. Verkhoturov, S.V. Nikolenko: Classification, development and creation of

electrode materials for electrospark alloying, Strengthening technologies and coatings, (Klassifikatsii, razrabotka i sozdanie élektrodnykh materialov dlya élektroiskrovogo legirovaniya), Uprochnyayushtie tekhnologii i pokrytiya, No. 2, pp. 13-22, 2010 (in Russian).

[23] T. Penyashki, G. Kostadinov, I. Mortev, E. Dimitrova: Microstructures and wear properties of WC, TiN, and TiC based cermet coatings deposited on 210Cr12 and 45 carbon steel by contactless electrospark process, Tribological Journal BULTRIB, Vol. 6, pp. 154-167, 2016.

[24] Pl. Petrov: Mechanical Characteristics and Structure of Gas-thermal Coatings form Powders on Ni Base PNKH-10 and PNKH-14 (1050-00 and 1060-00) at Gas-chemical Coating of Fuel Mixture from Propane-Butane and Oxygen. Proceedings of the Union of Scientists, Series 'Technical Sciences', pp. 67-71, 2017 (in Bulgarian).

[25] G. Barbezat, A.R. Nicol, A. Sickinger: Abrasion, Erosion and Scuffing Resistance of Carbide and Oxide Ceramic Thermal Sprayed Coatings for Different Applications, Wear, Vol. 162–164 (Part A), p. 529, 1993.

[26] M. Kandeva, I. Peichev, A. Dimitrova: Wear of composite coatings deposited through gasthermal super sound stream (hvof-process), Tribological Journal BULTRIB, Vol. 11, pp. 198-203, 2012.

[27] M.Oksa, E. Turunen, T. Suhonen, T. Varis, S.-P. Hannula: Optimization and characterization of high velocity oxy-fuel sprayed coatings: Techniques, materials and applications. Coatings, Vol. 1, No 1, pp. 17-52, 2011.

[28] V.N. Korenev, V.V. Barabash, A.V. Semenov: The Bonding Strength of Powder Coatings in Gas-flame Spraying with the Hydrogen–Oxygen Flame. Journal Welding International, Vol. 31, No. 4, pp. 333-336, 2017 (in Russian).

[29] V.N. Korenev, V. N. Khromov: Improving the Adhesion Strength of Gas-flame Coatings. In:Advanced Coating Technology: a Collective Monograph (Ed. A. V. Kiricheka). Spectrum Publishing House, Moscow, pp. 85–160, 2012 (in Russian).

[30] D. Alontseva, S. Missevra, A. Russakova: Characteristics of Structure and Properties of Plasma Detonated Ni-Cr and Co-Cr Based Powder Alloys Coatings: Journal of Materials Science and Engineering A 3. (1), pp. 41-49, 2013.

[31] L.M. Demidenko: *High-fire-resistant Composite Coatings*. Metallurgy, Moscow, 1979, p. 216 (in Russian).

[32] J.Schubert, Š. Houdková, M. Kašparová, Z. Česánek: Effect of Co content on the properties of HVOF sprayed coatings based on tungsten carbide. in Proceedings of 21st International Conference on Metallurgy and Materials – Metal 2012, Brno (Czech Republic), 23-25.05.2012, pp. 1086-1091.

[33] A.D Verkhoturov, I.A. Podchernyaeva, L.F.Pryadko, F. F.Egorov: *Electrode materials for electrospark alloying*, M. Nauka, 1988, 224 p. (in Russian)

[34] G.V.Samsonov, A.P.Epik: *Refractory coatings*, M. Metallurgiya, 1973,p. 400, (in Russian).

[35] K.A. Habib, D.L.Cano, C.T. Caudet, J. Bellés, P. Ortells: Influence of Al2O3 Particle Size on Microstructure, Mechanical Properties and Abrasive Wear Behavior of Flame-Sprayed and Remelted NiCrBSi Coatings. Journal of Materials Engineering and Performance, Iss. 4, pp. 1-10, 2017.

[36] M.A. Garrido, A. Rico, M.T. Gómez, J.E. Fernández-Rico, J. Rodríguez: Tribological and Oxidative Behavior of Thermally Sprayed NiCrBSi Coatings, Journal of Thermal Spray Technology, Vol. 26, No. 3, pp.517-529, 2017.

[37] S. Houdková, E. Smazalová, M. Vostřák, J. Schubert: Properties of NiCrBSi Coating, as Sprayed and Remelted by Different Technologies, *Surf. Coat. Technol.*, Vol. 253, pp. 14-26, 2014.

[38] F. Fanicchia, D.A. Axinte, J. Kell, G. Brewster, A.D. Norton: Combustion Flame Spray of CoNiCrAl coatings, Surface and Coatings Technology, Vol. 315, pp. 546-557, 2017. DOI: 10.1016/j.surfcoat.2017.01.070

[39] T. Penyashki, G. Kostadinov, D. Radev, M. Kandeva: Comparative studies of tribological characteristics of carbon steels with gas flame coatings from new multi-component carbide composite materials. oxidation communications, Vol. 42, No. 1, pp. 74–89, 2019.

[40] A.E. Kudryashov, A.Yu. Potanin, D.N. Lebedev, et al: Structure and properties of Cr–Al–Si–B coatings produced by pulsed electrospark deposition on a nickel alloy. Surface & Coatings Technology, Vol. 285, pp. 278–288, 2016.

[41] V.F. Labunets, L.G. Voroshnin, M. V. Kindarchuk: *Wear-resistant Boride Coatings*. Technique, Kiev, 1989, p. 158 (in Russian).

[42] G.V. Samsonov, I. M. Vinitskiy: *Refractory Compounds*. Metallurgy, Moscow, 1976.

[43] T. Penyashki, G. Kostadinov, M. Kandeva: Investigation of the properties of non-tungsten electro-spark coatings on high speed Steel, in Proceedings of BALTTRIB'2017 edited by prof. J. Padgurskase. Published by Aleksandras Stulginskis University.

[44] V.N. Khromov: Studies of wear-resistant electro-spark coatings with nanocrystalline and amorphous structures. Strengthening technologies and coatings, Vol. 72, No. 12, pp. pp. 18–21, 2010.

[45] I.S. Kuznetsov: Electro-sparking treatment with electrodes from amorphous and nano-crystalline alloys of cutting parts Tr. GOSNITI, T. 108, pp. 230–233, 2011.